

<p>98-334057/30 A60 E19 L03 FARH 96.12.11 HOECHST AG DE 19651439-A1 96.12.11 96DE-1051439 (98.06.18) C07C 47/546, 17/16, 22/04, 255/33, 331/04, C08G 61/00, C09K 11/06, C07F 9/28, C07C 265/08, 47/55, 45/29 Preparation of bi:aryl derivative - by reacting two aryl derivatives to give intermediate product and reducing, selectively oxidising or exchanging with (pseudo)halogen C98-103594 Addnl. Data: SPREITZER H, KREUDER W, BECKER H, KRAUSE J</p>	<p>A(1-A2, 1-E, 1-E2, 1-E6, 1-E10) E(7-D, 10-A14A, 10-A15A, 10-A15E, 10-B1B, 10-D1C, 10-E4, 10-J2B3) L(3-D1, 3-H4A)</p> <div data-bbox="958 210 1445 630"> <p>(I)</p> </div> <p style="text-align: right;">DE 19651439-A+</p>
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<div data-bbox="259 903 584 1197"> <p>(II)</p> </div>	<div data-bbox="1055 924 1315 1155"> <p>(III)</p> </div> <p style="text-align: right;">DE 19651439-A+/I</p>
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<p>98-334057/30</p> <div data-bbox="259 1491 584 1911"> <p>(IV)</p> </div> <p>Z = PO(OR¹)₂, PO(R²)₂ or P(R³)₃⁺A⁻; X = CH₂Z or CHO;</p>	<p>Y¹ - Y³ = CH or N; Z = Cl, Br, I, CN, SCN, NCO, PO(OR¹)₂, PO(R²)₂ or P(R³)₃⁺A⁻; Aryl = 4-14C aryl; R¹, R² = 1-20C alkyl or alkoxy where CH₂ group(s) can be substituted by O, S, CO, COO, OCO, NR⁴, (NR⁵R⁶)⁺a⁻ OR CONR⁷, H atom(s) can be substituted by F, CN, F, CL or 4-14C aryl optionally substituted by R¹; R¹-R³ = 1-20C hydrocarbon; R⁴-R⁷ = H or 1-20C hydrocarbon; A⁻ = anion or equivalent; m = 0-2; n = 1-5; X' = CH₂OH or COOR⁸; one of T and T' = Cl, Br or I or 1-12C perfluoroalkyl sulphonyl; the other one of T and T' = SnR₃ or BQ₁Q₂; Q₁, Q₂ = OH, 1-4C alkyl or alkoxy, phenyl optionally substituted by halogen or 1-4C alkyl or alkoxy, or halogen, or Q₁ + Q₂ = 1-4C alkylene dioxy optionally substituted by 1-4C alkyl; and R⁸ = H or 1-12C hydrocarbon.</p> <p style="text-align: right;">DE 19651439-A+/2</p>
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Also claimed are the above biaryl derivatives per se.

MORE SPECIFICALLY

$Z = \text{Cl, Br, CN, PO(OR}^1\text{)}_2, \text{PO(R}^2\text{)}_2 \text{ or P(R}^3\text{)}_3^+ \text{A}^-$; $\text{Y}^1 - \text{Y}^3 = \text{CH}$, Aryl = phenyl, 1- or 2-naphthyl, 1-, 2- or 9-anthracenyl, 2-, 3- or 4-pyridinyl, 2-, 4- or 5-pyrimidinyl, 2-pyrazinyl, 3- or 4-pyridazinyl, 2-, 3-, 4-, 5-, 6-, 7- or 8-quinoline, 2- or 3-thiophenyl, 2- or 3-pyrrolyl, 2- or 3-furanyl or 2-(13,4-oxadiazol)yl, $\text{R}^1 = 1\text{-12C alkoxy}$, $\text{R}^{2'} = 1\text{-12C alkyl or alkoxy}$, $m = 0 \text{ or } 1$ and $n = 1\text{-}3$.

USE

The biaryl derivatives are used in the preparation of polymers (claimed) which are useful as electroluminescence materials.

ADVANTAGE

Gives high purity.

PREFERRED PREPARATION

$\text{T} = \text{I, Br, Cl or 1-12C perfluoroalkyl sulphonate}$ and $\text{T}' = \text{QR}_1\text{R}_2$; $\text{X} = \text{COOR}^8$.

In step (B), the intermediate product (IV) is obtained by reaction with (i) LiAlH_4 , diisobutyl aluminium hydride, THF or toluene; (ii)

borohydrides; (iii) H in the presence of a catalyst; or (iv) Na or NaH.

In step (Ca), product (IVa) is obtained by oxidation with DMSO/oxalylchloride or either pyridinium chlorochromate or pyridinium chromate.

In step (Cb), product (IVb) is obtained by reacting with HCl or HBr or either thionyl chloride or thionyl bromide in a compound of formula (Ib) (I: $\text{X} = \text{Cl or Br}$).

In step (D), a compound of formula (Ib) is obtained by reaction with a trialkyl phosphate in a bisphosphate or formula (Ic) (I: $\text{X} = \text{PO(R}^1\text{)}_2$).

EXAMPLE

30.1 g 2-bromoterephthalic acid diethyl ester, 27.6 g K_2CO_3 , 140 ml toluene, 26.7 g 4-hexyloxyphenyl boronic acid and 1.16 g $\text{Pd(PPh}_3\text{)}_4$ were reacted at 85°C under Ar, followed by work-up to give 44.7 g 2-(4'-hexyloxyphenyl) terephthalic acid diethyl ester as a yellow-brown oil of purity 85%.

40 g of the product was treated with 5.3 g LiAlH_4 in 200 ml THF, followed by work-up to give 20.3 g 2,5-bishydroxymethyl-4'-hexyloxybiphenyl as colourless needles of purity above 98% and m.pt. $72.5\text{-}74^\circ\text{C}$.

200 mmol HBr in HAc was mixed with 12.6 g of the product. Work-up

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gave 16.9 g 2,5-bisbromomethyl-4'-hexyloxybiphenyl as a clear, honey coloured oil of purity above 98%.
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